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Orcin-Sulphon-Phthaleins
and
Trichlorphosphanil.

Dissertation
Presented to the Board of University
Studies of the Johns Hopkins University
for the Degree of Doctor of Philosophy

By
Joseph Elliott Gilpin.
1892.

54362

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Orcein-sulphon-phthaleins

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He also wishes to thank Drs. Moore, Raymond and Williams for instruction received from them.

Introduction

For several years investigations have been carried on in this laboratory upon the action of the phenols on ortho-sulphobenzoic acid and its acid ammonium salt.

The line of investigation has been of the same general character as that of Von Baeyer,[1] upon the action of the phenols on phthalic acid and its derivatives. Remsen and Saunders[2] found that when benzoylbenzene sulphonic acid was heated with concentrated sulphuric acid at 200° sulphobenzoic acid was formed. Bleicher studied this compound and found that it could be prepared also by heating ortho-sulphobenzoic acid

[1] Ann. Chem. 183, 202 ff
[2] Am. Chem. J. 3

with resorcin. In 1887, Thiel, working in this laboratory, the results being published in his dissertation studied the action of various reagents on sulfon-fluorescein and also the action of phenol, resorcin, and hydrochloric on the sulfo-benzoic acid and its acid ammonium salt. Although the results of this work were not entirely satisfactory on account of the great difficulty of separating the compounds yet the point to the conclusion that, in the case of resorcin, the products obtained contained respectively two four, and six molecules of resorcin. The most satisfactory results were obtained by the action of resorcin on the sulfo-benzoic acid and its acid

ammonium salts, and although no product has been obtained containing six molecules of urea. Those containing two and four molecules were made. The first urea linked was that which takes place between urea and acid ammonium oxalo-sulpho-benzoate are heated together.

Preparation of the acid ammonium salt of oxalo-sulpho-benzoic acid

50 grams of commercial saccharine were boiled with three molecules of acid (1 part concentrated acid to 2 parts water) in a Kjeldahl flask connected with an upright condenser for six hours. After cooling, the para-sulphamine benzoic acid, which crystallizes out in needles

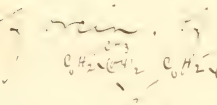
The commercial saccharine used which is not changed by the acid, being insoluble is separated by filtration. After evaporating to a small volume the solution is allowed to separate any deposit which consists of the ammonium salt and the insoluble substances. Another which occur in commercial saccharine in small quantities and which remain in the ammonium salt when the solution is evaporated to dryness. The solution is made alkaline with ammonia and some alcohol added. The acid ammonium salt crystallizes out in large crystals while the impurities remain in solution. The formation of the acid ammonium

Salt from the sulphonic-acid is in accordance with the following equations,

(1) $C_6H_4\langle^{CO}_{SO_2}\rangle NH + H_2O = C_6H_4\langle^{COOH}_{SO_2NH_2}$

(2) $C_6H_4\langle^{CO}_{SO_2}\rangle NH_4 + H_2O = C_6H_4\langle^{COOH}_{SO_2ONH_4}$

It was found that the action of urea on the acid ammonium salt would give a substance containing two molecules of urea, of this structure



whose formation could be represented in this way.

(1) $C_6H_4\langle^{COOH}_{SO_2ONH_4} = C_6H_4\langle^{CO}_{SO_2}\rangle NH + 2H_2O$

(2) $C_6H_4\langle^{CO}_{SO_2}\rangle NH + 2C_6H_3(CH_3)(OH)_2 = C_{21}H_{19}O_6SN + H_2O$

Action of Nitric Acid on Acid Ammonium Salt of Thio-sulpho-benzoic acid.

Nitric Acid was mixed with the acid ammonium salt in the proportions of 1 and 2 molecules of the acid to 1 of the acid ammonium salt. The product thus obtained was treated with Ether. Ether dissolved out the product which was then evaporated to dryness. The residue was then treated with water in which it dissolved. The water was then

The oxide of tellurium was used
The unsatisfactory method of Jannasch -
Von which consists in dissolving
the oxide in alkali and
reprecipitating again with acids, gave
excellent chances of obtaining
pure products. As no definite compound
could be obtained from this reaction
with the acid itself was next tried.

Interaction of tetra-sulphoxalic acid

The method used was that described by
Rose and Debray. The acid ammonium
salt was treated with twice its weight
of phosphorus pentachloride and the
two taken well together. After a short
time action began accompanied by a
copious evolution of hydrochloric acid gas.

(1) Am. Chem. J. 11, 332.

The product of this action is the chloride of the acid which is formed thus:

$$C_6H_4\begin{cases}COOH\\SO_2ONH_4\end{cases} + 2PCl_5 = C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 2POCl_3 + NH_4Cl + HCl.$$

After distilling off most of the oxychloride by action in a sulphuric acid bath, the chloride was washed well with cold water to remove the soluble products of the decomposition. Upon the addition of water a white substance is obtained which is probably the chloro-thiazhuret of nitrogen first made by Liebig and Wöhler, and afterwards studied by Gladstone and Holmes[2] and which like these investigators got in the combination $(PNCl_2)_3$. The formation of this compound is due to the action of the thiazhuric acid chloride on the ammonium chloride formed.

[1] Journ. Chem. Soc.
[2] Chem. Soc. Journ. 1862
[3] Liebig's Ann. 3 63

it is insoluble in water; but is volatile with water vapor so that most of it could be removed by distilling off a part of the water. After this had all been driven over an upright condenser was attached and the water was boiled until all the chloride was converted into the acid. This change takes place in this way:

$$C_6H_4\begin{matrix}COCl\\SO_2Cl\end{matrix} + 2H_2O = C_6H_4\begin{matrix}COOH\\SO_2OH\end{matrix} + 2HCl$$

The solution of the acid was evaporated to dryness and heated in a water-bath until free from hydrochloric acid. The acid is very deliquescent and should be kept in a vessel over sulphuric acid. If instead of the ammonium salt the potassium salt

is used in making the chloride the formation of the chlorosubstituted nitrogen is avoided. As the action of the phenols and the acid is essentially a dehydrating one. The resin used in these experiments was heated to 105° to drive off the molecule of water which it contains. The first experiment was that in which a nitro-resin was formed.

Action of resin on Picric-sulphuric-Sulphonic acid
Diresin-sulphon-sulphalein

Resin and the sulphuric acid a solution of the resin in the acid were well mixed and put in a short tube which was suspended in a sulphuric acid bath. A thermometer was used as a stirring rod in order that the

temperature might be regulated.
The temperature was about
70° at which point the resin melted
to a straw-yellow-colored liquid. The
acid dissolved in this as the tempera-
ture rose and at 160-170° water began
to come off. Constant stirring was kept
up the whole course of the action;
a precaution we in many cases
have found not to result in foul
ing. The color gradually turned to
dark red and after the mass had
become quite thick stirring was heated
to 180° until it was too stiff to stir.
If the melt is plunged into cold
water while still quite warm, the
material is entirely endolent, leaves
away from the glass and can be treated
without difficulty. After being

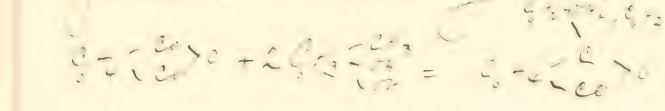
powdered it was washed well with the aid of the filter pump to remove any acid. The acid or alkali, and then dissolved in alkali. The coloring is obtained from the solution by adding hydrochloric acid when the material is precipitated as a flocculent mass. It was found much easier to wash this precipitate, if the liquid was first evaporated off and the mixture of the combined and sodium chloride well powdered. This was washed until all the sodium chloride was removed and the wash water showed no marked color. The dried material and dull in color. This powder produced in this way is a dark red color easily soluble in alcohol,

with a marked red and green fluorescence; nearly insoluble in water; and slightly soluble in alcohol and ether, in concentrating the solutions [illegible]. It always comes down as a zinc salt and shows no [illegible] crystalline form. Four [illegible] were made in this way using the same proportions; but only one of these came out chromatically pure. The general tendency seems to be towards the formation of the di and tetra- products mixed, whether the urein be present in the proportions of two or four molecules.

Fischer in his work on the action of urein on the bile acid anhydride found that one of the oxygen atoms was replaced by two urein residues, water being eliminated in the reaction. It

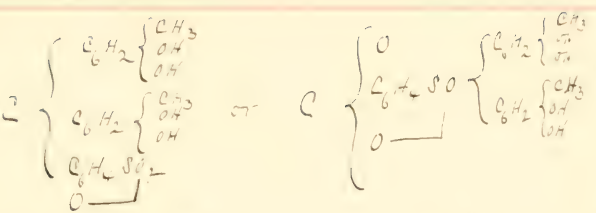
[illegible] Ann 189 53.

Represented in this way



It was asserted that with the ortho-hydroxybenzoic acid a similar action would take place leading to the formation of a diresin derivative of ortho-salicylic acid. From the work on this product it can hardly be doubted that diresin-salicylic acid is formed but in each case there is some triresin-salicylic acid formed at the same time. Mr. Baker found that in the action of resorcin on salicylic anhydride it was not the anhydride oxygen which was replaced, but as in the phenols, we should find the same

It holds good here; but a possibility presents itself in the case of the [illegible] in which the [illegible] is that we have said in the latter case it makes no difference which of the two [illegible] is replaced, the result will be the same; but with the nitro-sulpho-benzoic acid in which it is combined with [illegible] these combine with sulphur. Which of these possibilities is realized we cannot say, as we cannot tell how the [illegible] with the new residue is joined. Representing the benzoic-sulphonic acid as a derivative of toluene in the same way we would have the structure of the compound which was obtained by [illegible]



The results of the analyses were as follows:

Preparation I.

0.131 gram of the substance gave 1.0398 grams $BaSO_4$ (Liebig)

0.1752 gram of the substance gave 0.0707 gram H_2O and 0.3575 gram CO_2.

Preparation II

0.376 gram of the substance gave 0.0682 gram $BaSO_4$ (Liebig)

0.305 gram of the substance gave 0.1013 gram [illegible]

0.1 gram of the substance gave 0.0016 gram $BaSO_4$ (Liebig)

0.100 gram of the substance gave 0.0-70 gram [illegible]

0.1682 gram of the substance gave 0.0693 gram H_2O and 0.3732 gram CO_2.

0.2992 gram of the substance gave 0.1184 gram

.1926 and .0725 gram CO_2

Analysis II

.1926 gram substance gave 0.1484 gram $BaSO_4$ (Baker)

.145 gram of the substance gave .1002 gram H_2O and .330 gram CO_2

.173 gram of the substance gave 0.0715 gram H_2O and 0.396 gram CO_2

Analysis I

0.1128 gram of the substance gave .185 gram $BaSO_4$ (Baker)

	Calculated for $C_{21}H_{18}O_4S$ =		Found			
			II			
C	66.80	69.32	66.47	66.27	—	—
H	4.36	4.48	4.57	4.63	—	—
S	7.72	7.32	6.8	6.45	6.85	6.60

III		IV
62.47	62.78	—
4.82	4.66	—
7.13		6.90

The first of these was, when the method of reduction and sublimation is taken into consideration, comparatively pure diorcin-sulphon-phthalein. The others however contained amounts of carbon and sulphur which would correspond to mixtures of di and tetrabrom-sulphon-phthalein varying according to the proportions of each present but in general showing a greater tendency towards the tetrabromination. The tetrabromin sulphon-phthalein from this it was thought that a pure tetra product could be obtained by the use of more resin in proportion to the acid but it was found that this was not always true

Jetmorin - Sulphon - Solution

Urine and Albumen - Tryone and
in the Potassium four molecules
of the former before of the latter
were heated in a tube as in the
previous experiments. This mixture
melted at 81°-91° and almost immediately
became decolored. The temperature
was raised to 105° at which point water
began to recede and was kept there
until the solution had nearly ceased.
It was then raised to 175°-180° and
kept at that temperature until the
mass became too stiff to stir. This
took on an average about eight hours.
In two cases the tube cracked after
the operation was completed but
while the mass was in a soft

condition. The action in these cases seemed to be different from that in which the action was completed. This will be discussed more fully after the results of the analysis have been given. Four preparations were made under the same conditions as near as could be determined, except that two were not treated with lard. In each case they were well washed, dissolved in alkali and precipitated by acid then washed and dried as in the other cases.

Preparation E.

When this specimen had become dark the heating was stopped on account of the fact that the material was treated like the rest. The method of being all soluble in alkali

out about half. It was 20. Both the soluble and insoluble products were removed and were dark red in color.

Preparation II

This specimen was treated with cold alkali and was entirely soluble in alkali. When washed with hot water it formed a pasty mass which solidified on cooling. This powder was bright red.

Preparation III

The same accident happened in this case as in preparation I and the products were exactly the same except that the soluble part was yellow.

Preparation IV

This was similar to prep. I. but dark red.

The fusion = and = of $BaSO_4$ soluble salts in mixture number one from = and = with a citric mixture. The results of the analyses were as follows.

Preparation =. Soluble part.

0.1427 gram of the substance gave 0.0667 gram H_2O and 0.3393 gram CO_2.

0.2524 gram of the substance gave 0.1184 gram H_2O and 0.6039 gram CO_2.

0.2572 gram of the substance gave 0.1136 gram H_2O and 0.6258 gram CO_2.

0.1056 gram substance gave 0.0374 gram $BaSO_4$ ($LiCl$)

Preparation =.

0.1821 gram of the substance gave 0.0799 gram $BaSO_4$

0.1412 gram of the substance gave 0.0654 gram $BaSO_4$

0.2 gram of the substance gave 0.1008 gram $BaSO_4$

0.2 gram of the substance gave 0.1054 gram H_2O and 0.4803 gram CO_2.

This specimen was dissolved in aqua regia + reprecipitated by acid in order to purify it, and then analyzed for Lithium.

0.1520 gram of the substance gave 0.3730 gram $BaSO_4$ (Lithia)

Preparation — Lithia Earth.

0.2000 gram of the substance gave 0.3881 gram $BaSO_4$ (Lithia)

0.1338 gram of the substance gave 0.0621 gram $BaSO_4$ (Lithia)

0.1542 gram of the substance gave 0.1934 gram $BaSO_4$ (Lithia)

0.2083 gram of the substance gave 0.1145 gram H_2O and 0.5015 gram CO_2.

0.2328 gram of the substance gave 0.1226 gram H_2O and 0.5618 gram CO_2.

Preparation IV

0.1693 gram of the substance gave 0.0796 gram $BaSO_4$ (Lithia)

0.1315 gram of the substance gave 0.0613 gram $BaSO_4$ (Lithia)

0.1915 gram substance gave 0.1751 gram H_2O and 0.4580 gram CO_2

0.2222 gram substance gave 0.1077 gram H_2O and 0.5044 gram CO_2

The products obtained in the various [illegible] The oil and ether products on attempting [illegible] in ether gave on finding a difference in [illegible]. Although it was slightly soluble in alcohol the [illegible] was not determined. The same result was obtained as before.

0.2474 gram substance gave 0.1201 gram H_2O and 0.5624 gram CO_2

Calculation — and III. Insoluble part.

Nitrogen was found in the products.

0.1842 gram substance gave 0.0783 gram H_2O and 0.4265 gram CO_2

0.1848 gram substance gave 0.0803 gram H_2O and 0.4239 gram CO_2.

Calculated for

$C_{35}H_{32}N_4$

Found

Preparation I (Soluble)

C	85.21	84.84	85.37	85.66	—
H	6.46	5.19	4.83	4.89	—
N	11.33	—	—	—	11.56

Preparation II

C	84.43	—	—
H	5.22	5.13	—
N	5.99	6.35	6.45

Preparation II (Purified)

—	
—	
6.27	

Preparation III (Soluble)

85.65	85.80	—
5.12	5.17	—
11.23	11.42	7.31

Preparation II (Purified)

82.02	81.77
5.17	5.18
6.25	6.20

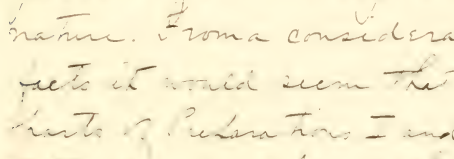
Preparation IV (Soluble)

85.75	85.35
5.12	5.17
9.13	9.48

Of these figures are studied in connection with the methods of separating the products. some very interesting facts appear

It would seem that when the heating was not continued until the substances became hard, two products were formed, one containing no sulphur and the other being the tetra product. The sulphur in Exp Exp was less than the theoretical but some there was due to a slight amount of the insoluble part which was present as an impurity. When the heating was continued until the mass became hard the product was not a tetra product, but most likely a mixture of the di and tetra compounds. Although attempts were made to separate these it was found that two products could not be obtained from the tetra by any means available

The amount of the insoluble material the product containing no sulphur, which was available was too small to permit of an investigation of its nature. From a consideration of these facts it would seem that the soluble resin of Preparations I and II were the tetrahydro-anthrol-anthralin whose structure regarding it as a derivation of Anthracene would be either



differing only in the position of the remaining reduced oxygen of the carbonyl group and one of those combined with anthracene both the oxygen atoms combined with anthracene.

Action of Phosphorus pentachloride on Tetramethylammonium Chloride

June 7 The residues were made in Portland to get a Tetra product were treated with Phosphorus pentachloride in order to replace if possible the hydroxyl group by chlorine and to gain some knowledge as to the number of hydroxyl groups present. These residues, drying, like the substances from which they were made crystal in character. On mixing some of the material with five times its weight of phosphorus pentachloride and heating for several hours a little to 150-160 Thionyl oxychloride hydrochloric acid and a pink mass was formed which was washed with water to remove all traces of phosphorus oxychloride

It is insoluble in water but in contact with it the colour changes to chocolate. Three three substances made in this way were analysed but the results did not conform to any calculated chlorine product nor did the agree with each other, so the action evidently did not give rise to the formation of one product.

Hexaoxin-sulphon-phthalein.

Attempts were made to obtain a third product, but they were unsuccessful. Although the temperature of the bath was not raised any higher than in the formation of the tetra product a deep seated decomposition seemed to have taken place as hydrogen sulphide was set free and the

products were entirely different from those formed in similar reactions.

It appears quite probable from this work that while dibrom-sulphon-phthalein and tetrabrom-sulphon-phthalein are formed in some cases, yet the hexabrom-sulphon-phthalein is not formed at all.

Inhaltsverzeichnis.

Trichlorphosphonitrile chloride.

Introduction.

The existence of chlorophosphonitrile, $(PNCl_2)_3$ as a by-product in the formation of ortho-sulpho-benzoic acid from commercial saccharine has directed our attention to this very interesting substance. Discovered by Liebig it was studied by Liebig and Wöhler,[1] Gladstone and Holmes,[2] Laurent,[3] Michaelis[4] and Stokmann.[5] The latter studied its action with aniline and paratoluidine and obtained derivatives in which the chlorine had been replaced by the residue of aniline and paratoluidine. The product with the aniline having the composition $P_3N_3(NHC_6H_5)_6$

1. Ann 11 139
2. Ann 76 [illegible]
   Chem Soc Jr (2) I 275
3. Compt. Rend 1850 [illegible]
4. Berichte 3 163
5. Berichte 1884 1910

the formation of the chlorochromate of nitrogen is due to the action of chromyl chloride on ammonium chloride. The possibility was suggested of obtaining a derivative of it by using methyl ammonium chloride, a substitution product resulting in trichloride. Although the compound obtained in this reaction is not a derivative of the chlorochromate of nitrogen still a comparison of the two forms an interesting study. Then also the tendency of chromic acid and nitrogen to combine sometimes in a very stable form, as in the chlorochromate of nitrogen, and in a substance obtained in this investigation which will be discussed later. The chlorochromate of nitrogen can be boiled with

concentrated acids and alkalies without undergoing change; but the nickel-ammonium chloride formed in this work is the most stable known with nearly all reagents, and often shows when heated to more than the work that has been done up to the present in the action of aniline on the chlorides of phosphorus has been misinterpreted. The action of aniline on phosphorus trichloride was studied with the trichloride. Fait obtained by the action of aniline on phosphorus trichloride a compound to which he gave the formula $P(NH_2C_6H_5Cl)_3$. Jackson and Menke [2] repeated this work; but were unable to obtain the compound described by Fait. They obtained a product which Fin-

[1] Zeitschr. 1855 648
[2] Amer. Chem. J. 6. 89.

Thomas[1] has PCl, to $C_6H_5NH_2$, but was unable to isolate it by dissolving it in alcohol and precipitating with water. They obtained $P(NHC_6H_5)_3$, which they considered its hydroxide. Meyer studied the action of aniline on the trichloride of arsenic and obtained two definite products by the successive substitution of the chlorine atoms by aniline residues obtaining $AsCl_2(NHC_6H_5)$ and $AsCl(NHC_6H_5)_2$. The third stage he was unable to accomplish. The trichloride of bismuth having the composition $BiCl_3(NHC_6H_5)_3$ which I have obtained in this investigation is in great similarity to the first derivation obtained by Meyer. They are very sensitive to moisture and

[1] Dissertation Bonn 89

decomposes with water and cleaned in a similar manner. After considerable experimenting the following method was adopted as the best for its formation

Preparation of Trichlorbenzidine.

Two grams trichloride and two grams dry aniline hydrochloride are mixed in molecular quantities, not more than ten grams of the aniline hydrochloride should be used at a time as the action takes place better with small quantities. The intimately mixed compounds are placed in a distilling flask and connected with a condenser tube at the lower end of the condenser passes into a vessel of water to absorb the hydrochloric acid and then the

cal of the retort. The bulb is then immersed in a sand bath and heat applied. When the temperature is reached at which the naphthalene sublimes a small quantity of glass wool is introduced into the upper part of the neck of the retort. The temperature is kept at 175° for six or eight hours, the naphthalene sublimed on the cool part of the bulb, and sometimes in the condenser, as a white crystalline mass which is easily removed. After the distillation of the naphthalene is complete the bulb is opened and the retort has cooled the material can be obtained in a very pure condition if the part in the neck of the bulb is discarded after being powdered

it is placed in a dessicator over caustic
potash to remove the hydrochloric
acid it must be kept perfectly dry
as it decomposes if exposed to moisture.
It cannot be purified by crystallization
as water decomposes the acetone and
other solvents decompose it in subli-
ming it also there was some decomposition
there remains a small quantity of a
dark green charry material in the bottom
of the sublimation tube the action is
then heated with water this results
violently at first in consequence
small excess of phosphorus pentachloride
and a tar like mass is formed which
is not acted on by water, alkali, and
dilute acids, and which solidifies
on cooling it is soluble in alcohol with
a green color it some was discolored in

method and precipitated by addition of water, filtered and washed. This process was repeated several times and the green powder obtained was analysed but different preparations varied in composition, and it was evidently not a single definite compound. The formation of the trichloro-derivative may be expressed in the following way.

$$PCl_5 + C_6H_5{\cdot}NH_2{\cdot}HCl = PCl_3(NC_6H_5) + 3HCl.$$

Concentrated sulphuric and nitric acids at 170° decompose it the former with the evolution of hydrochloric acid fumes and the other acts on it with evolution of hydrochloric acid and the generation of considerable heat. Sodium hydroxide acts on it to a slight extent and changes it to a hard brittle mass.

For titration with water it is recommended that hydrochloric and phosphoric acids and sodium hydroxide and phosphorus can be determined in the same electrolyte. The chloride is silver chloride and the phosphorus as magnesium pyrophosphate. It is evident that none of the hydrochloric acid was driven off during the titrations. Those were made by the Parsons method, and the agreed with those made in the Phosphate.

The following are the results of the analysis

Preparation I

0.3682 gram of the substance gave 0.7874 gram AgCl
0.2844 gram of the substance gave 0.5220 gram AgCl
0.2501 gram of the substance gave 0.4812 gram AgCl

1.3662 grams of the substance gave 1.344 grams H_2O and
1.2848 grams of the substance gave 1.130 grams H_2O and
1.2564 grams of the substance gave 1.242 grams H_2O and

1.2753 grams of the substance gave 0.1881 grams H_2O and 0.3195 grams CO_2

0.4078 grams of the substance gave 22 cc. Nat. N and 7.25 mm.

Preparation II.

1.2861 grams of the substance gave 0.4037 grams C.

0.3538 grams of the substance gave 0.6334 grams C.

1.3535 grams of the substance gave 1.094 grams H_2O and
0.4237 grams of the substance gave 28 cc. Nat. N and 7.2 mm.

0.3694 grams of the substance gave 0.0765 grams H_2O and
0.4081 grams CO_2.

0.3646 grams of the substance gave 0.0748 grams H_2O and
0.4037 grams CO_2

	Calculated for $PCl_3(NC_6H_5)$	Found	
		I	II
C	31.55	31.63	30.09 - 30.53
H	2.19	2.45	2.29 - 2.27
Cl	46.53	45.59 - 45.36 - 45.11	44.43 - 44.01
P	13.58	3.64 - 13.41 - 13.56	13.40
N	6.17	6.38	6.47

some new results have resulted from this research, by further experiments, and are fairly satisfactory, considering the difficulties of the work. The sulphate and nitrate of aniline were also treated with phosphorus pentachloride but they did not react. The hydrochloride of aniline with the nitrate was very violent taking place immediately the two were mixed in the cold. On heating the whole mass was carbonized in a short time. Para toluidine hydrochloride was also treated with phosphorus

tetrachloride without the formation of a volatile product.

Decomposition with water.

When the trichloride chloride is added to water it first melts and forms an oil which is decomposed by further boiling. The decomposition which takes place corresponds to the formation of aniline and hydrochloric acid & phosphoric acid. and can be represented thus

$$PCl_3(C_6H_5)_3 + 4H_2O = C_6H_5NH_2HCl + 2HCl + (C_6H_5)_3PO$$

After the decomposition with water the solution was evaporated and the crystals separated out, recrystallized and analyzed. The results of the analyses showed it to be aniline hydrochloride.

Another portion was decomposed with water and excess of barium hydroxide added to liberate the aniline and this then distilled off. After filtering off the excess of the hydroxide the presence of barium chloride was proved showing that the hydrochloric acid had been present. The barium was then treated with sulphuric acid and the chloric acid obtained by evaporating the solution.

Decomposition with alcohol

When the nickel-hydrazine is added to absolute alcohol a decomposition takes place with the evolution of hydrochloric acid. The action gives rise to considerable heat and the product is in solution

in Pinus sylvestris. The tracheal system is confined to the wood, in which the substance is contained which forms a somewhat viscous mass. This can be removed by water, but even at the ordinary temperature and hastened in a desiccator in which it forms an opaque and forms a solid mass. In the investigation of this substance seemed to offer difficulties on account of the lack of time during the season in which it was not studied enough to lead to any conclusions as to its nature.

Action of Trichloracetic acid on aniline

Ex. The trichloracetic acid is slowly added to boiling aniline. It is discolored and the aniline gradually loses its color. The addition is continued until crystals are seen on the sides of the flask after shaking it. If now this is allowed to cool it becomes solid with a mass of crystals. These crystals are insoluble in alcohol and can be separated from the rest of the material in that way. The insoluble crystalline product is not acted on by dilute acids or alkalies but very violently by fuming nitric acid. Several Brominations of this product were made and they agreed

in Trinidad but the results obtained were not sufficient to justify us in drawing any conclusion as to their value. Attempts were made to prepare substituted anilines and toluidines from their derivatives but as yet the have proved unsuccessful. The action of the reagents in the case of the bromo and nitro derivatives of the chlorine is reduced to aniline, but not a simple reduction. The result of the action of the reagents on the nitro-derivatives of the chlorine which is soluble in alcohol was extracted by adding water and dilute acid when it came down as a fine powder. It was washed and dried and

attempt made to analyse it. This led to a very interesting discovery. When this substance was burned with chromate mixture to determine the hydrogen and carbon, the percentage of carbon found was so small that it was thought that the all the carbon had not been burned. So some was heated in a boat.

It was then found that part of the substance was burned but that a considerable quantity of a glossy brittle black material remained. This could not be burned even by long continued heating in the blast lamp. This substance is very remarkable for its stability. Determinations of its constituents showed it to contain almost pure

nitrogen and carbon another sample of the substance & chlorine and nitrogen to form very stable compounds as in the chloroplatinate of nitrogen. The platinum was determined as magnesium pyrophosphate the substance having been decomposed with potassium hydroxide and potassium nitrate. There was no method that could be used to determine the nitrogen was the oxide but that could not be relied on as the other substances in this class lost part of their nitrogen. A results for five hours at red heat in a stream of oxygen the carbon was burned off (0.0050 gram.) The substance lost from this a small

quantity of a white substance was left. On the determination of the carbon in the rock residue an acrid smell, & a white substance which remained. A quantitative test showed that this contained considerable phosphorus.

The black stable residue is very similar to a product obtained by Rose by obtained by the action of phosphorus trichloride on ammonia a product he described as $PCl_3 + 5NH_3$. When this was heated ammonium chloride and ammonium chloride were formed and a white substance left which was Phosphon $= P_2N_3H$. The difference of this and the black residue is

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with the nitric. Neither are soluble in water or acids and are only partly decomposed by boiling with fuming nitric acid for some time. Concentrated sulphuric acid attacks the phosphor but acid potassium sulphate is necessary to decompose the black residue. Neither are acted on when heated in a stream of chlorine. They are decomposed by fused alkali and also with generation of phosphine on a compound of phosphorus and hydrogen when heated red hot in a current of hydrogen. The black residue may also contain a small amount of hydrogen but this cannot be considered as proved for the decomposition of the substance is

accompanied with so great a difference that the source of error mentioned may account for the presence of the cyclonea. Future work may show that it is closely related to the [illegible] which it so closely resembles in its actions towards reagents. Work will be continued on these substances and also on the action of the p-toluidene hydrochloride on the [illegible] which it is boiled will yield a substance related to the Benzhydrol.

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